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Rapid selective separation of americium/curium from simulated nuclear forensic matrices using triazine ligands

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Abstract: In analysis of complex nuclear forensic samples containing lanthanides, actinides and matrix elements, rapid selective extraction of Am/Cm for quantification is challenging, in particular due the difficult separation of Am/Cm from lanthanides. Here we present a separation process for Am/Cm(III) which is achieved using a combination of AG1-X8 chromatography followed by Am/Cm extraction with a triazine ligand. The ligands tested in our process were CyMe₄-BTPhen, CyMe₄-BTBP, CA-BTP and CA-BTPhen. Our process allows for purification and quantification of Am and Cm (recoveries 80%–100%) and other major actinides in < 2 d without the use of multiple columns or thiocyanate. The process is unaffected by high level Ca(II)/Fe(III)/Al(III) (10 mg mL⁻¹) and thus requires little pre-treatment of samples.

Keywords: Americium separation, nuclear forensics, triazine ligand, BTPhen, BTBP.

1 Introduction

Nuclear forensic techniques aim to characterise unknown radioactive materials to provide evidence for use in le-

gal cases, for example in seizures of illicit nuclear material. The collection of data must be performed in a timely manner and analytical techniques must be strategically applied to minimise sample loss/damage (*i.e.* non-destructive techniques applied first). Although the methodology of investigation will be driven by the specific sample, details of elemental and isotopic composition are required to allow comparison with reference data. This requires multiple analytical methods (*e.g.* radiometric methods, mass spectrometry) to be applied to the sample. However, samples in nuclear forensics can be complex, containing lanthanides, actinides and matrix elements, including fission/activation products with isotopic variation. Radiochemical separation is therefore required in order to avoid isobaric and polyatomic interferences (*e.g.* ²³²U/²³²Th) in mass spectrometry and/or spectral overlap in radiometric analyses [1–3].

The inability to obtain pure fractions of the lanthanides and Am/Cm is currently a bottleneck in nuclear forensic investigations of such samples. Pure solutions are necessary to avoid the interferences stated above and avoid problems in the electro-deposition and obtain a high quality data set for modelling. While some methods have been reported which achieve this in 1–2 d [4–6], these processes require multiple column steps and/or rely on the use of thiocyanate for Am elution, resulting in toxic wastes. More commonly, separation of Am/Cm and lanthanides from these complex samples requires a process which may take up to 7 d (Figure 1).

We envisaged a simplified process in which Am/Cm, actinides and lanthanides could be extracted and quantified from a complex nuclear forensic sample in < 2 d, whilst also avoiding the production of toxic waste. Specifically, this would entail separation of the major actinides (U(VI), Pu(IV), Np(IV)) by chromatography using current methods, followed by extraction of Am/Cm(III) from the remaining matrix containing lanthanides and matrix elements.

Multiple soft-N donor ligands based on 1,2,4-triazines have shown selectivity for complexation with Am/Cm(III) over other actinides and lanthanides, with

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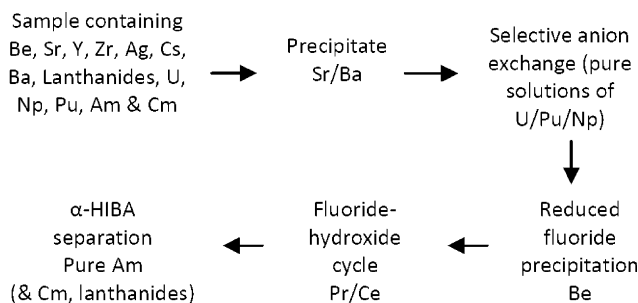


Fig. 1: Example of Am separation for a nuclear debris sample.

separation factors >100 [7]. This can be attributed to the enhanced covalency in bonds formed by the $5f$ orbitals of the actinides, which confers a preference for softer ligands [8]. In our process, we desired a decontamination factor of >1000 for Am/Cm(III), which could theoretically be achieved by ligands with such separation factors. Therefore, we identified four ligands based on the triazine motif for potential application in the extraction of Am/Cm(III) from a complex nuclear forensics matrix (Figure 2). Herein we report application of these ligands to the extraction of Am/Cm(III) from aqueous matrices containing lanthanides and matrix elements which are representative of complex nuclear forensic samples for the development of a rapid Am/Cm(III) separation process. The matrices applied contain lanthanides, actinides and matrix elements, including fission/activation products which simulate a complex sample. Subsequently we have also shown that a related ligand immobilised on the solid support (PVB-Me₄BTPPhen) is capable of Am separation from complex matrices [11].

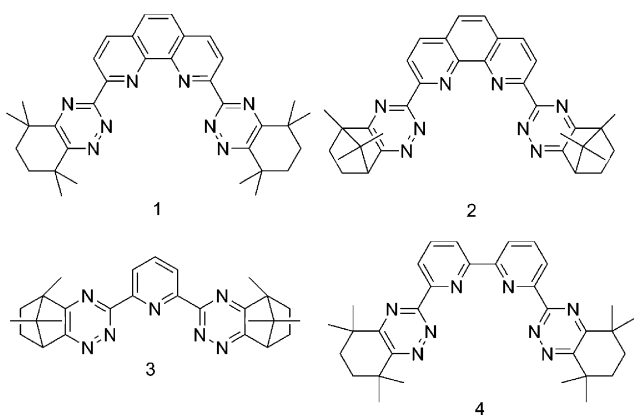


Fig. 2: Structures of the ligands used in this comparison study.

2 Experimental

All radionuclides used were provided from calibrated stocks in the School of Chemistry, University of Manchester. Micropipettes of 100 μ L, 0.1–1 mL and 2–10 μ L were calibrated on a 4 d.p. balance with >18 M Ω deionised water in the temperature range 18–22 $^{\circ}$ C and were found to be within their stated range. All acid solutions were made from analytical grade concentrated solutions and were diluted with >18 M Ω deionised water. All solutions were considered to have expired within one month of creation. Gamma counting was performed using a Canberra 2020 coaxial HPGe gamma spectrometer with an Ortec 919E multi-channel analyser. Gamma spectroscopy was performed against a standard of known activity counted in the same geometry and analysed using the diagnostic photon energies of ^{241}Am (59.5 keV) and ^{152}Eu (121.8 keV). Samples were electroplated and alpha spectrometry was performed on a Canberra model 7401VR detector with multi-channel analyser. ICP-MS analysis was performed on an Agilent 7500cx spectrometer. Multiple standards for each element in the range 1–100 ppb were used for ICP-MS quantification. All reagents and solvents used were of standard analytical grade unless otherwise stated.

2.1 Ligand synthesis

CyMe₄BTPPhen, CyMe₄BTBP and CA-BTP were synthesised as reported previously [12–14], and purified using the method reported by Whittaker *et al* [14]. CA-BTPPhen was synthesised using a modification of the previously reported procedure [15], in which the solvent was changed to EtOH and the reaction time changed to 3 h reflux followed by 6 h at RT. CA-BTP was purified in the same manner as the other three ligands. Data collected for all intermediates and ligands was as previously reported.

2.2 Am/Cm separation from normal nuclear forensics matrix

Generation of matrix: Using 4 M HCl (VWR, AnalaR NORMAPUR[®] grade) a solution containing ~ 1 mg mL^{−1} of metal was prepared by dissolving the following elements in the chloride form (Sigma-Aldrich or Fluka, $>99.99\%$ trace metal): Be(II), Cs(I), Mo(VI), Ce(III), Pr(III), Nd(III), Sm(III), Tb(III), Y(III), Zr(IV), Ag(I), Cd(II), Sr(II) and Ba(II). Spike solutions of ^{241}Am (III, 10–100 Bq range), ^{152}Eu (III, 10–100 Bq

range), ^{244}Cm (III, 10–100 Bq range), ^{232}U (VI), ^{239}Pu (IV) and ^{237}Np (IV, 10 Bq each isotope) were added and the solution readjusted to 4 M HCl. *N.B.* For high level Fe/Ca/Al matrices, the matrix was generated as above with the addition of $\sim 10\text{ mg mL}^{-1}$ Fe(III) or Ca(II) or Al(III), added as chloride.

Anion exchange/extraction chromatography: The matrix was evaporated to dryness twice times with addition of conc. HCl (2 mL). The residue was dissolved in the minimum volume of conc. HCl. A 50 mm \times 4 mm anion exchange column (Bio-Rad AG1-X8, 200–400 mesh) was conditioned with the following procedure: sodium bromate (5 mg) in conc. HCl (5 mL) was added. The column was washed with conc. HCl (4 mL) then aq. HCl (5 mL, 1 M) and conc. HCl (5 mL). The sample was loaded using conc. HCl to wash (2 mL). Am(III), lanthanides(III), Cs(I), Be(II) were eluted with conc. HCl (6 mL). Pu(III) was eluted with conc. HCl containing 1% v/v HI (5 mL). Co, Zr, Np(IV) were eluted with HCl (5 mL, 4 M). Mo, Fe, U(VI) were eluted with HCl (3 mL, 1 M) followed by HCl (3 mL, 0.5 M). Cd and Ag were eluted using deionised water (1 mL) followed by NH_4OH (4 mL, 1 M).

Liquid–liquid Am/Cm separation procedure: Each ligand was dissolved in 1 mL of 1-octanol to its chosen concentration, mixed for 5 min and sonicated for 1 min. The organic phase was contacted with the Am-containing fraction from chromatography for 90 min with vortex mixing. The sample was centrifuged at 1788 g/4000 rpm for 5 min and the phases separated. The aqueous phase was analysed by gamma spectroscopy and then evaporated to dryness, dissolved in aqueous HNO_3 (2% w/v, VWR, AnalaR NORMAPUR[®] grade) and diluted by a factor of 10 000 for ICP-MS analysis. The organic phase was back-extracted with 0.1 M HCl for 90 min and the resulting aqueous solution electroplated as below. The U, Pu and Np-containing fractions from chromatography were also electroplated for alpha spectrometry.

Electrodeposition procedure: The solution to be electroplated was evaporated to dryness. Aqueous NaHSO_4 (5%, 2.5 mL), water (2 mL) and aqueous Na_2SO_4 (15%, 5 mL) were added to the residue and heated, the solution was transferred to an electrodeposition cell using water (3 mL) and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (160 mM, 1 mL) was added. The current was set to 0.5 A for 5 min, then 0.75 A for 60 min. 1 min before the end of electrodeposition, aqueous KOH (25%, 2 mL) was added. The solution was decanted off and the cell washed with aqueous NH_4OH (5%, 2 mL). The plate was rinsed with 5% NH_4OH , ethanol and acetone before drying in the air.

3 Results and discussion

3.1 Ligand selection

The family of four ligands used in this study was based around $\text{CyMe}_4\text{-BTP}$ **1**, previously shown by us to separate Am/Eu with a separation factor of up to 400 [9]. We therefore identified $\text{CyMe}_4\text{-BTP}$ as a potential ligand for the separation of Am from aqueous matrices containing actinides, lanthanides and matrix elements. The ligand can be recycled for repeat use, and adheres to the CHON principle such that it can be safely incinerated after use, avoiding the generation of toxic waste. From this, we identified 3 related ligands with similar properties which could be applied to selective extraction of Am/Cm: CA-BTP **2**, CA-BTP **3** and $\text{CyMe}_4\text{-BTBP}$ **4** (Figure 2). These ligands encompass the most promising triazine motifs previously used in Am/Eu separation (BTPs, BTPHens and BTBPs). We also attempted to select compounds which could easily be obtained in an analytical laboratory setting *i.e.* easily synthesised. In particular, we were interested in ligands containing the camphor (CA) group as this is resistant to hydrolysis/radiolysis [12] and the camphor diketone required for synthesis is commercially available (unlike CyMe_4 diketone). CA-BTP **3** was chosen as a potential ligand as it is synthesised in only two steps and has increased solubility in 1-octanol compared to BTBPs and BTPHens [9]. CyMe_4BTBP **4** is the current benchmark ligand for the proposed SANEX process and has been widely applied to Am (III) extraction in recent years [8, 10].

3.2 Application of ligands to Am/Cm extraction from simulated nuclear forensic matrices

The four ligands were synthesised as previously reported [12–14]. Based on previously reported work, our work with the BTPHens ligands and preliminary Am/Eu(III) separations carried out as part of this investigation, we determined a number of parameters for the Am/Cm extraction. The organic phase selected for the separation was 1-octanol, since alternative solvents such as cyclohexanone were shown to cause phase separation issues in initial tests with the nuclear forensic matrix. The aqueous phase selected was 4 M HCl as this would be compatible with further separation processes *e.g.* for the lanthanides. Acid concentrations in the range 2–4 M (HCl or HNO_3) would be suitable for Am extraction from previous Am/Eu separation work [9]. We avoided the addition of phase modifiers in this work as this could

Table 1: Recoveries of eluted matrix elements from AGI-X8 column chromatography from analysis by alpha spectrometry and ICP-MS. (N.B. error calculated from instrument and method error plus one sigma, sample data averaged from $n = 20$ analysis of all run in triplicate).

	Isotope						
	⁹⁰ Zr	⁹⁵ Mo	¹⁰⁷ Ag	¹¹¹ Cd	²³² U	²³⁹ Pu	²³⁷ Np
Recovery±	97.21	95.23	99.74	92.01	96.76	97.24	96.08
Error/%	±2.01	±1.99	±1.05	±1.35	±3.21	±2.12	±0.71

increase co-extraction of particular elements such as lanthanides, and also complicate back extracted. (N.B. Separation factors (Am/Eu) were determined to be similar to those reported above, for distribution ratio data and HCl/HNO₃ extraction data please see [9, 12, 13]).

The simulated nuclear forensic matrix was designed to simulate an aqueous acidic matrix obtained from a nuclear debris sample after pre-treatment (e.g. total dissolution). The matrix was generated by dissolution of Be(II), Mo(VI), Cs(I), Ce, Pr, Nd, Sm, Tb, Y (all III), Zr(IV), Ag(I), Cd(II), Sr(II) and Ba(II) and all the lanthanides (except Pm and Eu) as chlorides in 4 M HCl solution. The target concentration for each stable element was $\sim 1 \text{ mg mL}^{-1}$ of metal. Tracers of ²⁴¹Am(III), ¹⁵²Eu(III), ²⁴⁴Cm(III), ²³²U(VI), ²³⁹Pu(IV) and ²³⁷Np(IV) were added and the solution adjusted to 4 M HCl. The concentration of each element in the representative matrix before Am/Cm(III) extraction was determined by ICP-MS.

The simulated nuclear forensic matrix was then subjected to AGI-X8 anion exchange chromatography (chloride form) to separate the major/minor actinides (U(VI), Pu(IV), Np(IV)) and yield an Am/Cm(III) containing fraction which would be used in the subsequent triazine ligand extraction. The major actinides were analysed by alpha spectrometry and recoveries were found to be >94% (Table 1). Recoveries of the co-eluting matrix elements (Zr, Mo, Ag, Cd) were determined by ICP-MS of the relevant fractions and found to be >91% (Table 1). This first step of the overall separation process allows for immediate separation of the major actinides, allowing their quantification (electrodeposition and alpha spectrometry) to be performed concurrently with the subsequent Am/Cm(III) separation. This would ensure data is collected in a timely manner, which is of vital importance in nuclear forensics.

The Am/Cm(III) fraction was then subjected to liquid-liquid separation using each of the four ligands in 1-octanol/4 M HCl. The phases were vortex mixed for 90 min, this was based on the time required for Am/Eu (III) extraction using CyMe₄BTPhen in our previous work. The resulting aqueous phases were analysed by gamma spectrometry (to determine Eu) and ICP-MS analysis (to determine matrix elements). The organic phase was back-extracted with 0.1 M HCl for 1 h (determined in preliminary work to be adequate for consistent back extraction) and the resulting aqueous phase was analysed by alpha spectrometry for Am/Cm. Extraction of Am and Cm(III) was seen with all four ligands (Table 2). CyMe₄BTPhen extracted the highest quantity of Am(III)

Table 2: Recoveries of eluted matrix elements for AGI-X8 column chromatography/triazine ligand separation from analysis by alpha spectrometry, gamma spectroscopy and ICP-MS. (N.B. error calculated from instrument and method error plus one sigma, sample data averaged from $n = 20$ analysis run in triplicate, all calibrated against a range of standards in the concentration ranges above).

Ligand	Isotope recovery ± error/%						
	²⁴¹ Am	²⁴⁴ Cm	¹⁵² Eu	⁹ Be	⁸⁸ Sr	⁸⁹ Y	¹³³ Cs
CyMe ₄ -BTPhen	96.4 ± 2.3	94.1 ± 2.2	95.0 ± 4.1	98.2 ± 2.2	99.7 ± 0.7	98.7 ± 2.4	100.1 ± 2.0
CA-BTP	70.0 ± 2.2	65.0 ± 2.3	90.8 ± 6.2	98.2 ± 2.6	99.2 ± 2.1	93.2 ± 0.5	91.9 ± 2.5
CyMe ₄ BTBP	85.7 ± 2.6	95.2 ± 2.8	95.3 ± 3.9	99.8 ± 1.0	94.5 ± 1.1	99.8 ± 1.9	95.2 ± 0.6
CA-BTPhen	43.5 ± 2.7	56.1 ± 2.6	93.8 ± 5.6	99.9 ± 0.8	92.9 ± 3.1	92.2 ± 0.5	101.3 ± 2.1
	¹³⁷ Ba	¹³⁹ La	¹⁴⁰ Ce	¹⁴¹ Pr	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁵⁷ Gd
CyMe ₄ -BTPhen	99.0 ± 1.0	94.4 ± 0.5	95.2 ± 2.1	99.6 ± 1.7	100.6 ± 2.1	102.1 ± 1.0	99.2 ± 1.5
CA-BTP	99.6 ± 0.8	93.7 ± 1.0	96.4 ± 1.2	100.3 ± 1.0	97.7 ± 1.0	94.3 ± 0.7	99.1 ± 0.3
CyMe ₄ BTBP	101.0 ± 1.1	102.1 ± 2.8	100.0 ± 1.3	99.6 ± 0.7	98.9 ± 1.1	107.2 ± 9.7	100.1 ± 0.7
CA-BTPhen	91.9 ± 0.3	94.7 ± 1.0	88.7 ± 0.6	92.5 ± 0.7	94.7 ± 0.6	99.3 ± 0.3	99.7 ± 0.4
	¹⁵⁹ Tb	¹⁶³ Dy	¹⁶⁵ Ho	¹⁶⁶ Er	¹⁶⁹ Tm	¹⁷² Yb	¹⁷⁵ Lu
CyMe ₄ -BTPhen	94.6 ± 1.2	94.3 ± 1.5	98.9 ± 0.5	91.6 ± 1.0	97.7 ± 0.3	98.9 ± 1.2	95.1 ± 1.2
CA-BTP	97.8 ± 0.6	98.2 ± 1.1	98.9 ± 0.7	97.6 ± 0.7	101.7 ± 0.7	97.8 ± 0.5	91.3 ± 2.1
CyMe ₄ BTBP	97.4 ± 0.2	100.5 ± 1.3	98.9 ± 0.6	99.2 ± 1.2	99.3 ± 0.2	100.5 ± 1.6	100.3 ± 0.9
CA-BTPhen	98.2 ± 0.2	99.7 ± 0.5	98.7 ± 0.4	95.8 ± 0.4	97.4 ± 0.4	99.9 ± 0.4	102.4 ± 2.2

Furnaced and leached complex nuclear forensic sample – aqueous matrix of Be, Sr, Y, Zr, Ag, Cs, Ba, Ln, U, Np, Pu, Am, Cm (& Fe/Ca/Al)

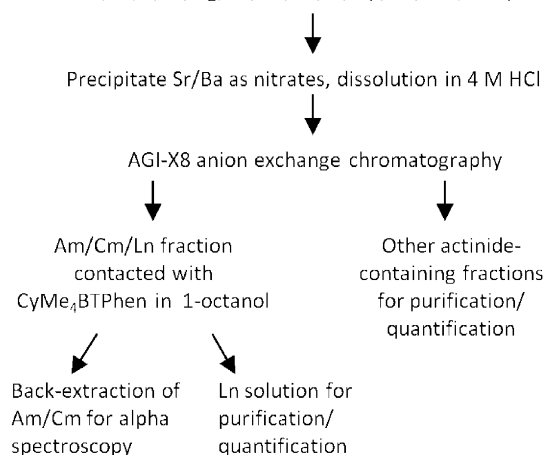


Fig. 3: Method for extraction of Am/Cm from complex nuclear forensic sample using CyMe₄BTPhen (this work).

over 90 min ($96.0 \pm 2.3\%$) and also had high extraction of Cm(III, $94.1 \pm 2.2\%$). The other three ligands extracted Am/Cm(III) to a lesser extent over 90 min, but when the mixing time was increased to 3 h these recoveries were $>90\%$. Over the 90 minute separations, Eu (III) extraction was minimal compared to Am/Cm(III) extraction. ICP-MS analysis showed high recovery of matrix elements including all lanthanides (III, $>88\%$, Table 2) showing that the method allows for high decontamination (and $SF > 100$ for each ligand with respect to the lanthanides) for Am/Cm with respect to these elements.

Overall, the combined AG1-X8/triazine ligand separation procedure developed allows for the quantification and determination of the major actinides (U, Pu, Np) and Am/Cm(III) within 2 days. In addition, a lanthanide containing fraction is obtained which can be subjected to further separation. From the results obtained, CyMe₄BTPhen is the most promising ligand for a rapid extraction (<90 min) of Am/Cm. We therefore propose a method, as shown in Figure 3, in which this ligand is utilised for Am/Cm(III) extraction from a Am/Cm/Ln solution post AG1-X8 chromatography.

3.3 Am/Cm extraction from simulated nuclear forensic matrices in the presence of Fe, Ca and Al

Complex nuclear forensic samples may be derived from any origin, but Fe, Ca and Al are often present in high amounts as these elements are found in high amounts in

soils, cements and metals. Typically samples with high levels of these elements require additional purification to avoid interference with separation processes. We wished to assess the impact of (10 mg mL^{-1}) Fe, Ca and Al on our Am/Cm separation procedure. We therefore generated three matrices by separate addition of Fe(III), Ca(II) and Al(III) in chloride form to the matrix described above, and repeated the investigation with each of the four ligands. With sampling we felt that these levels would simulate matrix element interferences.

Recovery of U(VI), Np(IV), Pu(III), Zr(IV), Mo(VI), Ag(I) and Cd(II) from AG1-X8 chromatography was unaffected by high levels of Fe, Ca or Al, as expected. Iron was also removed in this part of the process (co-eluted with U, separated by precipitation), with a recovery $>93\%$ by ICP-MS across all experiments (errors from SD from $n = 14$ replicates $< 3.0\%$ in all experiments). After extraction of Am/Cm by the four ligands, the remaining elements were determined as previously, also Ca and Al were determined by ICP-MS (Table 3). Am/Cm and Eu extraction was unaffected for all ligands in the presence of Ca and Al except for CyMe₄BTBP in the presence of Ca when Am/Cm extraction was reduced by $\sim 15\%$ – 20% . Recovery of matrix elements including lanthanides was not greatly affected by the presence of high level Ca or Al. From ICP-MS analysis, the recoveries of Ca and Al were also determined from each separation. Apart from CA-BTPhen, all ligands were seen to co-extract both Al and Ca to some extent. In particular, for CyMe₄BTBP, Ca was extracted ($\sim 15\%$) and Am/Cm extraction decreased, meaning that high Am/Cm recovery could not be obtained even over a 3 h extraction. However, in cases where Ca(II)/Al(III) co-extraction does not affect Am/Cm(III) separation it will affect electrodeposition of the sample. In addition, pre-treatment steps could be utilised to remove the high level elements, but this could be at the expense of process time.

From investigation of the normal and high level Fe, Ca and Al matrices, we concluded that CyMe₄BTPhen is the most suitable ligand for Am/Cm(III) extraction from complex nuclear forensic samples based on the near-quantitative Am/Cm(III) extraction achieved in 90 min. In addition, high levels of Ca and Al did not affect the Am/Cm extraction by this ligand. To fully determine the ability of CyMe₄BTPhen to extract Am/Cm from complex nuclear forensic matrices, we then wished to perform the extraction in the presence of all elements *i.e.* without prior AG1-X8 chromatography.

Table 3: Recoveries of eluted matrix elements for high Ca (a) and high Al (b) from AGI-X8 column chromatography from analysis by alpha spectrometry, gamma spectroscopy and ICP-MS. (N.B. error calculated from instrument and method error plus one sigma, sample data averaged from $n = 20$ analysis run in triplicate, all calibrated against a range of standards in the concentration ranges above).

(a) Isotope recovery \pm error/%											
Ligand	^{241}Am	^{244}Cm	^{152}Eu	^9Be	^{88}Sr	^{89}Y	^{43}Ca	^{133}Cs	^{137}Ba	^{139}La	^{140}Ce
CyMe ₄ -BTPhen	95.9 \pm 2.4	93.9 \pm 2.4	95.2 \pm 6.5	99.2 \pm 2.1	98.8 \pm 3.2	95.7 \pm 1.9	96.4 \pm 1.2	107.6 \pm 1.2	98.3 \pm 1.0	98.9 \pm 1.0	92.5 \pm 1.3
CA-BTP	68.0 \pm 2.6	63.1 \pm 2.6	90.3 \pm 6.6	100.0 \pm 1.6	94.6 \pm 1.5	100.8 \pm 3.0	91.8 \pm 3.2	99.3 \pm 1.8	89.6 \pm 2.2	92.5 \pm 1.0	87.2 \pm 1.5
CyMe ₄ -BTBP	68.6 \pm 2.3	73.6 \pm 2.9	91.4 \pm 5.7	99.7 \pm 2.5	95.2 \pm 0.3	99.7 \pm 0.7	85.1 \pm 1.2	95.7 \pm 0.7	93.8 \pm 1.1	97.1 \pm 1.0	96.3 \pm 0.4
CA-BTPhen	41.5 \pm 2.4	43.4 \pm 2.2	95.3 \pm 6.8	99.7 \pm 1.3	93.5 \pm 1.2	102.8 \pm 0.9	103.0 \pm 2.3	102.3 \pm 2.6	100.5 \pm 1.5	102.9 \pm 1.2	100.9 \pm 0.6
(b) Isotope recovery \pm error/%											
Ligand	^{241}Am	^{244}Cm	^{152}Eu	^9Be	^{88}Sr	^{89}Y	^{27}Al	^{133}Cs	^{137}Ba	^{139}La	^{140}Ce
CyMe ₄ -BTPhen	94.8 \pm 2.1	97.8 \pm 2.1	95.0 \pm 6.2	98.8 \pm 1.3	98.4 \pm 0.7	98.4 \pm 1.9	86.5 \pm 2.2	92.7 \pm 1.2	92.1 \pm 1.0	94.3 \pm 1.1	97.6 \pm 1.3
CA-BTP	65.4 \pm 2.7	63.6 \pm 2.7	91.3 \pm 5.9	98.2 \pm 1.6	91.8 \pm 1.3	100.6 \pm 1.4	92.5 \pm 1.6	91.8 \pm 1.8	94.5 \pm 1.8	97.5 \pm 1.0	96.0 \pm 1.5
CyMe ₄ -BTBP	84.5 \pm 2.3	94.2 \pm 2.7	94.6 \pm 6.0	99.8 \pm 0.7	99.9 \pm 0.8	99.1 \pm 1.1	84.3 \pm 2.2	98.8 \pm 0.7	87.3 \pm 1.1	91.5 \pm 1.0	86.2 \pm 0.3
CA-BTPhen	43.5 \pm 2.7	53.1 \pm 2.7	101.4 \pm 5.9	99.8 \pm 0.9	100.0 \pm 0.6	93.6 \pm 0.9	100.5 \pm 0.8	102.9 \pm 3.2	100.6 \pm 1.5	101.7 \pm 1.8	95.6 \pm 0.6
(c) Isotope recovery \pm error/%											
Ligand	^{141}Pr	^{146}Nd	^{147}Sm	^{157}Gd	^{159}Tb	^{163}Dy	^{165}Ho	^{166}Er	^{169}Tm	^{172}Yb	^{175}Lu
CyMe ₄ -BTPhen	96.9 \pm 0.5	99.2 \pm 0.5	102.1 \pm 2.4	103.7 \pm 3.9	102.9 \pm 3.1	100.3 \pm 1.0	96.8 \pm 0.8	100.5 \pm 0.7	100.3 \pm 0.7	100.7 \pm 0.8	92.7 \pm 0.5
CA-BTP	91.3 \pm 1.1	93.0 \pm 0.9	97.0 \pm 1.6	97.4 \pm 0.6	95.3 \pm 1.3	96.9 \pm 1.4	99.8 \pm 1.7	93.1 \pm 1.0	100.7 \pm 1.3	99.9 \pm 1.7	92.1 \pm 2.0
CyMe ₄ -BTBP	96.0 \pm 1.9	93.3 \pm 1.4	100.4 \pm 1.6	94.2 \pm 2.4	100.1 \pm 1.4	94.2 \pm 0.5	96.4 \pm 1.1	89.5 \pm 1.4	97.2 \pm 0.7	87.0 \pm 3.0	101.1 \pm 2.1
CA-BTPhen	99.7 \pm 0.8	100.1 \pm 1.6	100.5 \pm 0.7	99.0 \pm 1.6	99.9 \pm 0.4	102.3 \pm 2.5	102.4 \pm 2.7	99.0 \pm 0.5	96.7 \pm 0.5	99.3 \pm 0.5	101.9 \pm 2.1
(d) Isotope recovery \pm error/%											
Ligand	^{141}Pr	^{146}Nd	^{147}Sm	^{157}Gd	^{159}Tb	^{163}Dy	^{165}Ho	^{166}Er	^{169}Tm	^{172}Yb	^{175}Lu
CyMe ₄ -BTPhen	101.8 \pm 2.1	99.0 \pm 0.3	96.5 \pm 0.5	91.7 \pm 0.6	96.0 \pm 0.3	96.9 \pm 1.0	92.8 \pm 0.8	98.9 \pm 0.7	100.2 \pm 0.8	97.5 \pm 0.5	98.0 \pm 0.9
CA-BTP	96.7 \pm 1.1	94.0 \pm 0.9	93.2 \pm 1.0	95.1 \pm 0.5	92.7 \pm 1.3	93.2 \pm 1.4	97.3 \pm 1.7	94.9 \pm 1.0	97.9 \pm 2.0	102.2 \pm 1.9	101.3 \pm 1.2
CyMe ₄ -BTBP	89.3 \pm 1.4	91.6 \pm 1.4	94.8 \pm 1.6	95.8 \pm 1.2	94.2 \pm 1.4	95.3 \pm 0.5	98.3 \pm 1.1	91.5 \pm 1.4	93.5 \pm 0.6	99.2 \pm 0.6	99.9 \pm 0.6
CA-BTPhen	99.1 \pm 0.8	98.1 \pm 0.9	95.2 \pm 0.7	99.6 \pm 0.3	98.2 \pm 0.4	100.4 \pm 0.5	101.0 \pm 1.8	99.4 \pm 0.5	99.5 \pm 0.5	97.3 \pm 0.5	91.4 \pm 0.5

3.4 Am/Cm extraction from simulated nuclear forensic matrices by CyMe₄BTPhen without prior chromatography

CyMe₄BTPhen was used to extract Am/Cm(III) in the manner outlined above from the normal matrix and matrices with high level Fe, Ca and Al, without the AGI-X8 chromatography method. Am/Cm(III) extraction was unaffected with recoveries >90% within 90 min, with minimal extraction of Eu(III) (Table 4). Recoveries determined for matrix elements including lanthanides by ICP-MS were >88%, including Ag(I) and Mo(VI) which were removed by AGI-X8 in our previous investigation. A notable exception is Cd(II), which was co-extracted from all matrices by CyMe₄BTPhen (recoveries 35%–45% depending on matrix). This can be rationalised as the closely related N-donor ligand 2,9-di(2-pyridyl)-1,10-phenanthroline has been shown to be a highly selective sensor of Cd(II) [16]. Although in our proposed AGI-X8/CyMe₄BTPhen extraction procedure this would not pose a problem as Cd would be removed in the chromatography step, Cd (II) can also be selectively removed from the Am/Cm solution using

known separation techniques [17]. For the high level Fe, Ca and Al matrices, recoveries of Fe(III), Ca(II) and Al(III) were >86% by ICP-MS (Table 4).

After separation, the aqueous phase was subjected to chromatography to separate U (VI), Pu (III) and Np (IV) for determination by alpha spectrometry. Recoveries >90% were obtained for the major actinides indicating presence of these elements does not affect Am/Cm(III) extraction. Overall, the initial method of AGI-X8/CyMe₄BTPhen separation would be preferred in order to simplify the matrix and avoid Cd (II) co-extraction, however this investigation shows that CyMe₄BTPhen may be used to extract Am/Cm in the presence of many competing ions with minimal co-extraction.

4 Conclusions

We have developed a selective radiochemical separation process for Am/Cm(III) for application to complex nuclear forensics samples using AGI-X8 chromatography followed by a triazine ligand extraction. In our procedure, purification and quantification of all major actinides can be achieved in >2 days, which would be valuable in a nuclear

Ligand: CyMe ₄ BTPhen, Isotope recovery \pm error/%						
Matrix	²⁴¹ Am	²⁴⁴ Cm	¹⁵² Eu	⁵⁶ Fe	⁴³ Ca	²⁷ Al
Fe(III)	91.3 \pm 2.3	90.2 \pm 2.3	95.1 \pm 5.1	100.1 \pm 3.1	—	—
Ca(II)	90.9 \pm 2.4	91.0 \pm 2.5	100.3 \pm 4.1	—	91.0 \pm 0.4	—
Al(III)	90.1 \pm 2.1	90.5 \pm 2.2	94.3 \pm 4.5	—	—	88.9 \pm 2.5
	⁹ Be	⁸⁸ Sr	⁸⁹ Y	⁹⁵ Mo	¹⁰⁷ Ag	¹¹¹ Cd
Fe(III)	99.1 \pm 4.4	100.5 \pm 1.6	86.6 \pm 1.4	100.0 \pm 0.4	100.8 \pm 0.8	44.7 \pm 0.4
Ca(II)	98.1 \pm 1.4	98.8 \pm 3.7	95.7 \pm 1.1	102.1 \pm 1.1	98.6 \pm 1.0	36.3 \pm 1.0
Al(III)	98.8 \pm 2.1	98.4 \pm 3.2	98.4 \pm 1.9	98.1 \pm 0.3	92.8 \pm 0.7	34.7 \pm 1.9
	¹³³ Cs	¹³⁷ Ba	¹³⁹ La	¹⁴⁰ Ce	¹⁴¹ Pr	¹⁴⁶ Nd
Fe(III)	98.4 \pm 1.1	88.2 \pm 0.3	90.3 \pm 1.4	94.3 \pm 1.0	96.4 \pm 1.2	90.4 \pm 1.1
Ca(II)	98.3 \pm 1.2	98.3 \pm 0.5	98.9 \pm 1.5	92.5 \pm 0.8	96.9 \pm 0.9	99.2 \pm 1.2
Al(III)	92.7 \pm 1.2	92.1 \pm 1.0	94.3 \pm 1.1	97.6 \pm 1.3	101.8 \pm 2.0	99.0 \pm 0.3
	¹⁴⁷ Sm	¹⁵⁷ Gd	¹⁵⁹ Tb	¹⁶³ Dy	¹⁶⁵ Ho	¹⁶⁶ Er
Fe(III)	100.8 \pm 0.9	94.2 \pm 0.7	92.9 \pm 0.7	93.8 \pm 0.6	88.6 \pm 1.1	94.2 \pm 0.8
Ca(II)	102.7 \pm 2.9	101.1 \pm 1.3	101.9 \pm 2.0	100.6 \pm 1.1	96.8 \pm 1.8	100.5 \pm 1.2
Al(III)	96.5 \pm 0.5	91.7 \pm 0.6	96.0 \pm 0.7	96.9 \pm 1.0	92.8 \pm 0.8	98.9 \pm 0.9
	¹⁶⁹ Tm	¹⁷² Yb	¹⁷⁵ Lu	²³² U	²³⁹ Pu	²³⁷ Np
Fe(III)	91.9 \pm 0.7	96.7 \pm 0.7	100.6 \pm 0.7	96.4 \pm 3.2	96.3 \pm 2.0	96.0 \pm 0.7
Ca(II)	100.3 \pm 1.5	100.8 \pm 1.0	92.7 \pm 0.8	96.1 \pm 3.3	98.5 \pm 2.2	95.4 \pm 0.6
Al(III)	99.5 \pm 0.7	97.5 \pm 0.8	98.0 \pm 0.5	96.7 \pm 3.3	98.5 \pm 2.1	92.6 \pm 0.7

Table 4: Recoveries of eluted matrix elements for high Al/Ca/Fe initial CyMe₄BTPhen (10 mM, 90 min) separation of nuclear forensic matrix, analysis by alpha spectrometry, gamma spectroscopy and ICP-MS. (*N.B.* error calculated from instrument and method error plus one sigma, sample data averaged from $n = 5$ analysis run in triplicate, all calibrated against a range of standards in the concentration ranges above).

forensics investigation. Our method avoids use of multiple column techniques and generation of thiocyanate waste. All four triazine ligands tested were found to extract Am/Cm from the matrix after AGI-X8 chromatography with little complexation of competing ions.

CyMe₄BTPhen was the best ligand for the procedure, as the improved Am/Cm extraction kinetics allow recoveries >90% to be obtained in 90 min. However, we believe all four ligands tested would be viable alternatives, and many are more easily accessed synthetically which may be of benefit to application in an analytical laboratory.

Overall, our investigation shows that these triazine ligands are capable of extracting Am/Cm from complex nuclear forensic matrices, including those with high level Fe, Ca and Al. We hope that this work can be utilised in nuclear forensic investigations and in the wider field of analytical radiochemistry to provide a new rapid method for Am/Cm separation.

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